Supplementary Information

1. Origin of intensity variations with isotopic substitution and relevance to combined data-set analysis.

A data-set is made of a number of points, i, and the intensity calculated at a particular point, y_{ci} is given by equation 2:

$$y_{ci} = s\sum_{K} L_K \left|F_K\right|^2 \phi(2\theta_i - 2\theta_K)P_K A + y_{bi} \qquad (1)$$

where s is the scale factor, L_K contains the Lorentz, polarisation and multiplicity factors, F_K is the structure factor for the Kth Bragg reflection, ϕ is the reflection profile function, P_K is a preferred orientation function, A is the absorption factor and y_{bi} is the background intensity at the ith point. The structure factor is given by equation 2:

$$F_K = \sum_{j} N_j b_j \exp[2\pi i(hx_j + ky_j + lz_j)]\exp[-M_j] \qquad (2)$$

where h, k and l are the Miller indices, x_j, y_j and z_j are the positions of the jth atom of the unit cell, M_j is the thermal displacement function, N_j is the site occupancy multiplier of the jth atom (site occupancy divided by the site multiplicity) and b_j is the scattering length of the jth atom.

From equations 1 and 2 it is readily apparent that by changing b_j for a particular atom the structure factor for the Kth reflection is altered along with the resultant calculated intensity at point i, if all other aspects of the structural model are unchanged. Equations 1 and 2 also give an insight into the origin of parameter correlation in a Rietveld refinement. N_j, M_j and y_{bi} are highly correlated such that the derived F_K from equation 1 will have a set of solutions with different values of N_j and M_j that will depend on the determined value of y_{bi}, which is also a multi-term, non-linear function. This is also true to a lesser extent for atomic positions. In complex refinements (*e.g.* site disordering, non-stoichiometry, low symmetry and models with large numbers of crystallographically distinct atoms) there are not enough fully resolved or resolvable Bragg reflections, K, to de-couple the

correlations between parameters, which lead to lower precision in, and also accuracy of, the final derived structural model. That is to say that the basis of the Rietveld method involves dividing the observed intensity between each contributing F_K and background and as the amount of reflection overlap increases this process becomes inherently less accurate.

Through the use of isotopic substitution a new set of resolved Bragg reflections are generated, K', for every isotope sample, with all other standard aspects of the structural refinement identical as the method assumes sample equivalence (peakshape, atomic positions, thermal displacements, site occupancies and instrumental parameters). This information effectively reduces the ratio of resolved peaks to variable parameter required for a high-precision study by de-coupling parameter correlations and so leads to a more accurate and precise structural model at any given level of complexity compared with a single data-set refinement.

2. Rietveld Refinement Strategy.

The practicalities of modelling the different scattering lengths of the isotopes require that each sample be entered as a different phase in the refinement, so that the scattering length of the constituent isotopes can be defined as each element can only have a single value for its neutron scattering length. Each phase is then hard constrained to be identical crystallographically. As each sample is prepared under identical conditions, the major peak-shape parameters (Gaussian and Lorentzian) are also constrained to be identical between phases, although particle size, strain and broadening parameters are allowed to vary independently. The phase fractions are then defined so that only the phase with the correct isotope scattering lengths contribute intensities at each observed data point in the data-set. This is achieved by manual manipulation of the crystal phase fractions of each phase to make the ratio 10^5:1 (*i.e.* unwanted phases contribute 0.001% of total scattering at any particular data point), although this figure is somewhat arbitrary.

The single data-set refinements were carried out without any atomic constraints. The fractional occupancies of the oxygen and copper atoms were kept constant at 1.0. The displacement parameters were initially modelled isotropically but in the final cycles were allowed to vary anisotropically. The variables in the final cycle were: background (5 term shifted Chebyshev polynomial), zero point (1), scale factor (1), lattice parameters (4), peak-shape parameters (3), oxygen positional parameter (1), anisotropic Cu displacement (6) and anisotropic O displacement (4) – giving a total of 25 variables. At each temperature point the final model from the previous temperature point was used as the initial model with the displacement parameters converted back to the U_{eq} isotropic values.

In the combined data-set refinement, each of the three phases was entered with hard constraints on the thermal parameters, oxygen position, lattice parameters and the peak-shape. The fractional occupancies of the Cu and O positions were fixed throughout the refinements at 1.0. In keeping with the single data-set refinements, the displacement parameters were initially varied isotropically before being allowed to vary anisotropically in the final cycles. In each of the three histograms, the background (3×5 term shifted Chebyshev polynomial), zero point (1×3) and scale factor (1×3) were allowed to vary independently (21 variables); the lattice parameters (4), peak-shape parameters (3), oxygen positional parameter (1), anisotropic Cu displacement (6) and anisotropic O displacement (4) were allowed to vary subject to the hard constraints described previously, giving a total of 39 variables.

Therefore, the total number of structural variables is identical in the single and combined data-set refinements, illustrating the use of a single crystallographic model. As with the single data-set refinements, the final model from the previous temperature point was used as the starting model for the next temperature point with the displacement parameters converted back to the U_{eq} values.